Materials Research Laboratory, Inc.

22333 Governors Highway ♦ Richton Park Illinois ♦ 60471
PIlgrim 8-8777 ♦ Chicago telephone ♦ PUllman 5-4020

FINAL REPORT

on

ELEVATED TEMPERATURE STRESS CORROSION OF HIGH STRENGTH SHEET MATERIALS IN THE PRESENCE OF STRESS CONCENTRATORS

Contract NASr-50

for

Office of Research Grants and Contracts

Code ~~BG~~ .,c

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington 25, D. C.

November, 1965

by

E. J. Ripling, R. L. Kirchner, R. P. O'Shea and R. G. Lingwall

N66-16193 N66-16195

(ACCESSION NUMBER) (THRU)

44 1

(PAGES) (CODE)

CR69851 17

(NASA CR OR TMX OR AD NUMBER) (CATEGORY)

FACILITY FORM 602

GPO PRICE $

CFSTI PRICE(S) $

Hard copy (HC) 2.00

Microfiche (MF) .50

ff 653 July 65

Materials
Research
Laboratory,
Inc.

22333 Governors Highway ♦ Richton Park Illinois ♦ 60471
PIlgrim 8-8777 ♦ Chicago telephone ♦ PUllman 5-4020

FINAL REPORT

on

ELEVATED TEMPERATURE STRESS CORROSION OF HIGH STRENGTH SHEET MATERIALS IN THE PRESENCE OF STRESS CONCENTRATORS

Contract NASr-50

for

Office of Research Grants and Contracts

Code BG

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington 25, D. C.

November, 1965

by

E. J. Ripling, R. L. Kirchner, R. P. O'Shea and R. G. Lingwall

Materials Research Laboratory, Inc.

MRL

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS, Continued

LIST OF ILLUSTRATIONS, Continued

INTRODUCTION

This report is written in three parts; each part describes a different aspect of research on the mechanism of hot salt stress corrosion cracking of titanium alloys.

Part I describes a study of the corrosion products formed on titanium in the presence of hot solid salt. Its purpose was to determine whether or not the corroding medium that causes cracking is a gas. It is shown that cracking is not caused by a gas but results either from a lowering of surface energy due to a creeping solid corrosion product or it results because hydrogen ions enter the metal in the course of the reaction.

Part II describes an investigation of the electrochemical aspects of the stress corrosion cracking. It shows that cracking occurs only at the cathode of an oxygen differential cell. Anodic protection of the specimen is able to prevent cracking.

Part III describes a number of miscellaneous experiments such as X-ray diffraction identification of corrosion products. None of these studies are sufficiently complete to be discussed in detail, however.

Materials
Research
Laboratory,
Inc.

M R L

6

N66-16194

PART I

THE DIFFUSION OF CORROSION PRODUCTS IN HOT SALT STRESS-CORROSION CRACKING OF TITANIUM

ABSTRACT

16194

An experimental technique is described for separating the gaseous, liquid and solid reaction products generated by the hot salt corrosion of titanium. By use of this procedure, it is shown that the product that causes cracking is not a gas, and hence would not be expected to be washed away by a fast moving air stream in service.

Author

INTRODUCTION

Titanium base alloys combine good corrosion resistance with a high strength-to-weight ratio and high toughness in the temperature range of 400 to 800°F. This outstanding combination of properties at elevated temperature coupled with a reasonable ease of fabrication, makes this class of materials the most promising for the skin of supersonic transports. When such aircraft operate at Mach 3, the equilibrium skin temperatures vary from approximately 450 to 600°F due to aerodynamic heating, and these temperatures increase with speed as a second-power function of Mach number (1).

In the presence of hot salt, however, titanium alloys may be less attractive since they suffer from stress corrosion cracking, at least under laboratory testing conditions, at the high end of this temperature range. In spite of this vulnerability to cracking when salt coated specimens are exposed to stress at temperatures above approximately 600°F, no service failures have been attributed to salt, even though many components of jet engines operate under conditions where such cracking would be expected (2). It has been suggested that this inconsistency between laboratory tests and the reported service behavior results because the small scale tests are not a true model of service conditions. In laboratory tests, salt coated specimens are generally hung in a creep furnace where volatile products, e.g. Cl_2 or HCl, generated by the reaction of Ti with NaCl, can collect, and attack the grain boundaries. Under service conditions, a fast air stream would wash away these products. This difference between trapping the corrosion products in stagnant air versus washing them away has been used to explain the difference in service and laboratory behaviors. Because of its prohibitive expense no attempts have as yet been made to duplicate the air stream in laboratory controlled tests. Nevertheless, in one experiment, it was shown that the formation of the corrosion product was not altered by the direction of air flow. In a 65 hour test at 900°F, an air flow of 2,000 ml/min. over a salt bead deposited on unstressed titanium resulted in a concentric pattern of corrosion products with no evidence of eccentricity in the direction of wind velocity (3). This experiment is not pertinent to cracking, however, since corrosion and attack by a secondary gas may not be affected in the same fashion by the moving air stream.

Obviously, predicting the serviceability of titanium alloys in specific high temperature application such as SST skins requires knowledge of the physical forms of the product that causes cracking. This project was undertaken to develop this needed information.

TEST PROCEDURE

In order to separate the gaseous corrosion products from liquids and solids, advantage was taken of the fact that the former will diffuse across an air gap while the latter two will not. To use this behavior difference, a testing technique was developed in which the corrosion products were produced on an unstressed portion of a test specimen which was separated from the stressed region in part by an air gap, and in another part by a metal bridge. The specimen was a typical sheet tensile sample with side hooks added to its two edges as shown in Fig. 1-a. When such a sample is loaded in tension, the hooks remain stress free.

With this specimen shape, a salt slurry was placed on the hooks where corrosion would occur. The various reaction products then migrate away from the salt bead in a fashion that identifies their physical form. If the cracking medium were a gas, it could most easily migrate across the air gap so that one would expect cracks to initiate anywhere in area (A) shown in Fig. 1-b. The extra finger marked "F" was added to the test specimen so that the stress concentration would be symmetrical about the salt bead. Hence, if a stress concentrator encouraged cracking, a gaseous corrosion product would produce cracks with equal ease at points P_1 and P_2. Liquid or solid reaction products must diffuse along the surface of the arm to reach the stressed portion of the test sample. Consequently, if the cracking medium were a liquid or a solid, one would expect cracks to occur at the intersection of the hook and stressed body of the sample, point P_1, Fig. 1-c.

A plastic model was made of the hooked sample, Fig. 2, in order to evaluate the stress concentration at the base of the prongs by photoelastic means. The prongs on the right side of the sample were made to have a generous radius, and on the left, the junction points were as sharp as could be made in the cast plastic model. It is apparent from the series of pictures in Fig. 2 that the stress at the base of the filleted prong is no higher than in the body of the sample, whereas if the sharp prongs are used the heavily stressed volume of metal would be smaller than can be detected in this model. Nevertheless, the stress at points P_1 and P_2 are identical for either shaped prong.

The hooked specimen separates gases from solids and liquids. A second technique was used for separating solids and gases from liquids. For this purpose a bead of salt was placed on the stressed section of a specimen of the type shown in Fig. 3-a. The specimen was then observed from its back side, i.e. with the salt bead out of view of the microscope so that the crack and corrosion products that traveled through the crack could be observed without interference from the unreacted salt. In viewing from the reverse side, liquid corrosion products would tend to collect at the tip of the crack due to capillary action so that the stain would be dumbbell shaped about the crack, Fig. 3-b. Solids and gases diffusing through the crack would develop elliptical stain patterns on the back side of the specimen, as shown schematically in Fig. 3-c.

All test samples were prepared in the same fashion. They are first metallographically polished over the section that is to be viewed followed by acetone wash to remove organic materials after which the specimens are soaked in an Alconox (detergent) solution. The specimens are then washed in distilled water, followed by an acetone rinse and dried. The salt used in most of the test series was natural sea salt obtained by evaporating sea water until the water content was reduced to form a paste with the consistency of tooth paste. The slurry was then applied to the test samples and dried at approximately 300°F until the bead appeared dry. After drying, the specimen was heated to the test temperature, the load applied, and the test started.

Over the time interval from the application of load until the first crack was detected, the movement of corrosion products was recorded by lapsed time still color photography. For ease in reproduction the photographs are shown in black-and-white in this report.

To carry out these tests a special tensile hot stage was designed. A schematic drawing of a cut section of the stage and a photograph of it are shown in Fig. 4. The device is described in greater detail in a separate publication (4). In order to control temperature, a thermocouple bead was held in contact with the side of the specimen away from the heater. The control couple was calibrated by welding a number of very fine thermocouple wires directly onto the specimen. It was found that the specimen temperature was actually about 50°F higher than the control indicated. Nevertheless, because welding might have changed the corrosion characteristics of the titanium, the use of mechanical attachment was continued. The same couple and method of attachment was used for all tests so that even though absolute temperatures were not precisely known, the temperature was identical for all tests.

For most of the tests, the hot stage chamber was open to the atmosphere, but because there was only one opening, the rate of air flow was modest. The amount of water vapor in the stage was determined by the thoroughness with which the salt was dried prior to testing. It became apparent in the course of the study, however, that moisture exerted a large influence on the diffusion rate of the corrosion products. Consequently, in one pair of tests "wet" or "dry" atmospheres were used. For these, the stage was closed excepting for a controlled inlet and exit air passage. The air for these tests was supplied from a compressed air cylinder.

The inlet air for the wet test was passed through a gas dispersion tube, but this did not supply a high enough moisture content so that a small water container and heater were added to the inside of the hot stage. The water in the container was maintained at a constant level by a float operating an external solenoid which in turn controlled a valve in the water line. The moisture content was determined by passing the exit air through a DRIERITE ($CaSO_4$) column and flow meter. By measuring the increase in weight of the DRIERITE and controlling the flow rate at 20 to 40 ml/min., the ratio of water to air was found to be 1.8 to 2.8 parts water/100 parts air.

The same flow rate was used in the dry tests, but for these, the DRIERITE column was placed on the inlet side of stage which, according to the manufacturer's literature, reduced the entering air to a dew point of $-100^{\circ}F$ ($<$10 ppm).

TEST RESULTS

Location of crack initiation around salt

Prior to using the hooked samples, salt slurries were placed on the body of polished and etched test pieces. These samples were dried, heated and loaded, and cracks began to form at the periphery of the salt bead, as shown in Fig. 5. Close examination showed a gray reaction product surrounding the bead, and it was within this area that the cracks were initiated. The observation that cracks are initiated only at the salt-titanium-air interface with heavy coatings is consistent with the results previously reported on creep samples (3) (5).

Diffusion of corrosion products

Over twenty tests have been made at the time of this writing with specimens with side hooks. The specimens were either Ti-6Al-4V or Ti-8Al-1Mo-1V. The salt in all cases, excepting where noted, was natural sea salt.

A typical test result on a hooked specimen is shown in Fig. 6. Shortly after the specimen attains its test temperature a blue stain moves from the salt bead along the surface of the side hook. In some cases, the blue stain also formed across the side hook, indicating that it may be produced by a gas. A gray stain follows on top of the blue one, traveling only along the metal arm, never across the air gap. When the latter reached the stressed body of the sample, a crack formed at the hook-stressed section intersection as shown in the bottom photograph. Cracking of all the specimens occurred only at this location. In no case was a crack found across the air gap from the bead indicating that the cracking medium is either a liquid or solid that has a high rate of surface diffusion on titanium. Cracking was almost entirely intergranular although some branches could also be found running through the grains, Fig. 7.

The Ti-8Al-1Mo-1V alloy appeared to crack after a shorter time at temperature than the Ti-6Al-4V alloy. The most important variable in controlling cracking time, however, was the moisture content of the air surrounding the test specimen. In one pair of tests the influence of a "wet" vs. "dry" atmosphere was compared by use of the technique described above. Lapse time photographs of the diffusion of the corrosion products are shown in Fig. 8, the wet test on the left and the dry one on the right. Both specimens used sea salt as the corroding medium. Note that after an hour, the blue stain in the wet test reached the stressed portion of the specimen. In an additional nine hours, the gray stain that is thought to cause cracking had traveled the full length of the side hook and a crack developed at the hook-stressed section intersection.

Similar results were obtained by using reagent grade NaCl rather than natural sea salt. The diffusion rate was somewhat slower, probably because of a slightly lower water vapor content in the sodium chloride tests. Measurement of the moisture content exiting the hot stage chamber gave an average of 2.8 parts of water/100 parts air in the sea salt experiment and 1.8 parts in the sodium chloride run.

For the dry test an identical salt slurry was applied to the hook, and dried at 300 $^{\circ}$F in air for 67.5 hours. For the first hour after attaining the test temperature, the blue stain moved rather rapidly from the bead, but the diffusion rate was then very slow for the remainder of the test. Presumably the initial fast diffusion resulted because the salt was not thoroughly dried before heating to the test temperature. Cracking finally occurred after approximately 150 hours at temperature, i.e., it required 15 times as long in the dry test as in the wet one for cracking to occur. For these two tests it was also possible to obtain diffusion rate data by measuring the location of the interface as a function of time, and it was found that diffusion occurs roughly 40 times as fast in a wet atmosphere as in a dry one.

In the course of the tests with hooked samples, attempts were made to distort the interface of the gray corrosion product by means of a probe. These were unsuccessful, however, implying that the surface diffusion product is a solid and not a liquid.

To be certain that the cracking medium was a solid rather than a liquid, a test was also conducted in which the salt slurry (a bead 5 to 10 mils in diameter) was placed on the side out of view of the microscope using a smooth tensile sample of Ti-6Al-4V alloy. Hence, the crack initiated on the reverse side of the sample and propagated through the specimen thickness and into the sight of the viewer.

Shortly after this test began, a crack formed and propagated through the thickness of the specimen into sight, Fig 9-a. As the crack width increased, the characteristic blue stain formed elliptically about the crack. Shortly afterward a smaller gray pattern developed around the center of the crack until a series of concentric ellipses delineated various thicknesses of corrosion product that had radiated from the salt bead, Fig 9-b and c. This corrosion product had the same appearance as the material with the high surface diffusion rate discussed above. The tip of the crack showed no concentration of corrosion product as would be expected if it were a liquid. When the heating element behind the specimen was brought up to a red glow, the inside of the crack could be readily observed and it appeared to be empty.

The experiment with the hooked sample discussed above showed that the corrosion product was either a solid or a liquid. The experiment now being described indicated it to be a solid or a gas, implying that it is, indeed, a solid. Liquid reaction products would tend to collect at the crack tip in an experiment of this type. To illustrate this phenomenon, the sample temperature in the above mentioned experiment was raised to the vicinity of the melting point of sea-salt. As the sample was heated to 1120°F, a meniscus could be seen forming in the crack, while at the same time a volatile product was given off that clouded the quartz window of the hot stage. After maintaining the melting temperature for fifteen minutes and subsequently cooling the sample for examination, spots of salt were found at each crack tip proving that a liquid corrosion product would concentrate in the narrowest regions of a crack due to capillary action.

DISCUSSION AND CONCLUSIONS

The fact that all hooked titanium specimens cracked only at the hook-stressed section intersection shows that titanium alloys in the presence of hot solid salt are not cracked by a gaseous reaction product such as Cl_2 or HCl. Hence, it cannot be expected that cracking will be prevented by washing away the generated gases in a fast moving airstream.

Either one of two mechanisms appear possible to account for the embrittlement. Since the specimens invariably crack after the gray corrosion product has reached the stressed section of the specimen, cracking may result from a lowering of the surface energy of the titanium as the solid corrosion product diffuses over its surface. This mechanism suggests that titanium alloys in the presence of hot salt cracks by a mechanism identical with that thought to occur in liquid metal embrittlement (6).

A second possibility is that hydrogen ions are produced by the corrosion, and these caused delayed failure. If the hydrogen ions are absorbed by the metal in the hook, a diffusion gradient would drive it down the arm and it would first encounter a stressed region at the location where cracks occur. In any event, since the hydrogen is present as an ion and not a gas it would not be eliminated by a fast moving air stream. Attempts to find an increased level of hydrogen in the salt induced fracture surfaces has not been successful.

REFERENCES

1. Raring, R. H., Materials Research and Standards, Vol. 3, No. 10, 1963, p. 810.

2. Boyd, W. K., and Fink, F. W., The Phenomenon of Hot Salt Stress-Corrosion Cracking of Titanium Alloys, NASA Contractors Report, NAPA, CR-117, October 1964.

3. Kochka, E. L., and Peterson, V. C., The Salt Corrosion of Titanium Alloys at Elevated Temperatures, Final Technical Report, Crucible Steel Company, January 1961.

4. Kirchner, R. L., and Ripling, E. J., A Tensile Hot Stage for Metallographic Examination, to be published, The Review of Scientific Instruments.

5. Kirchner, R. L., and Ripling, E. J., First Interim Report on Elevated Temperature Stress Corrosion of High Strength Sheet Materials in the Presence of Stress Concentrators, Contract NASr-50, November 1964.

6. Rostoker, William, McCaughey, Joseph M., and Markus, Harold, Embrittlement by Liquid Metals, Reinhold Publishing Corporation, 1960.

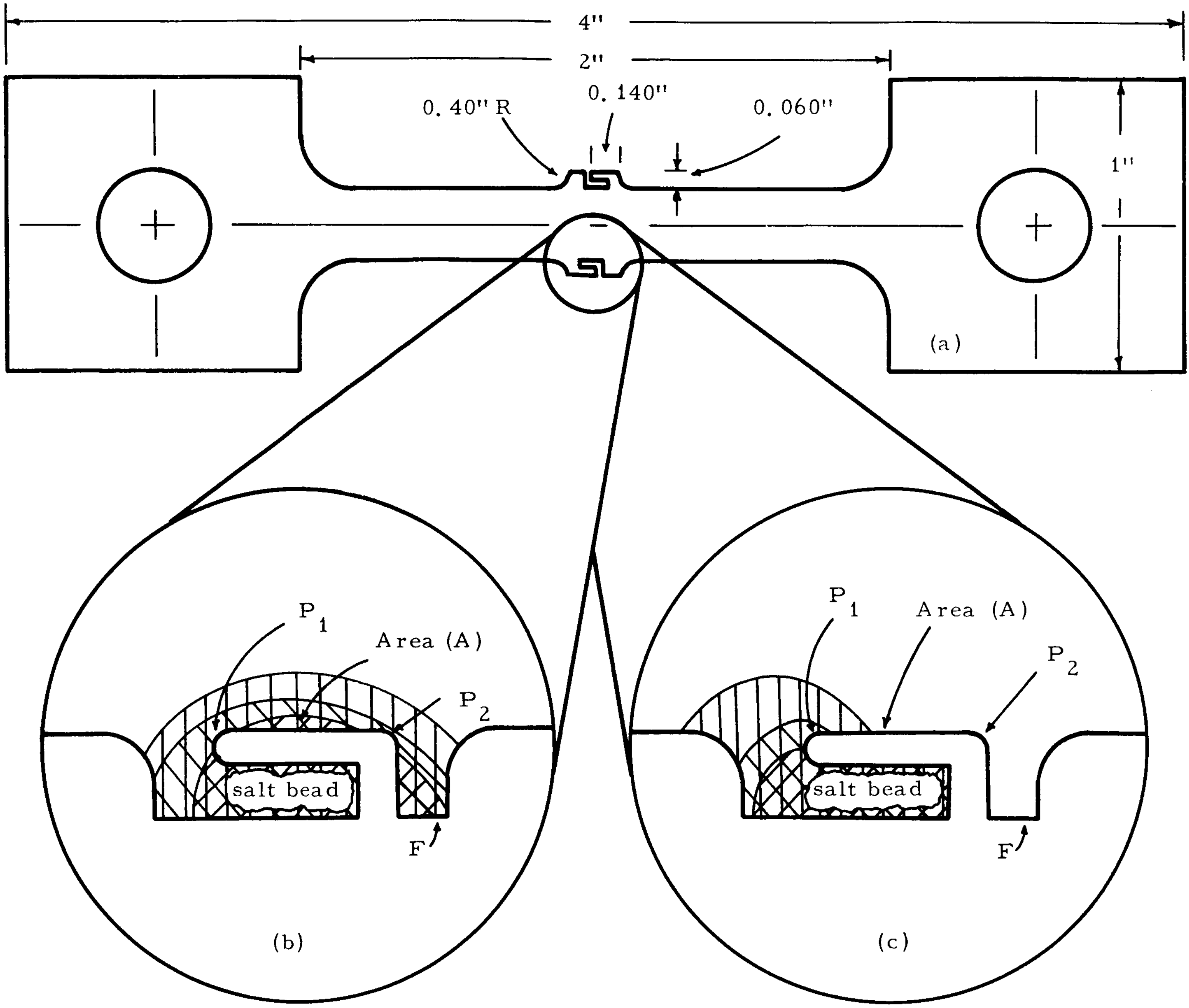


Fig. 1 (a) SIDE HOOKED SPECIMEN USED FOR GENERATING CORROSION PRODUCT AWAY FROM STRESSED AREA.

(b) EXPECTED STAIN PATTERN FROM GASEOUS CORROSION PRODUCTS.

(c) EXPECTED STAIN PATTERN FROM SOLID OR LIQUID CORROSION PRODUCTS.

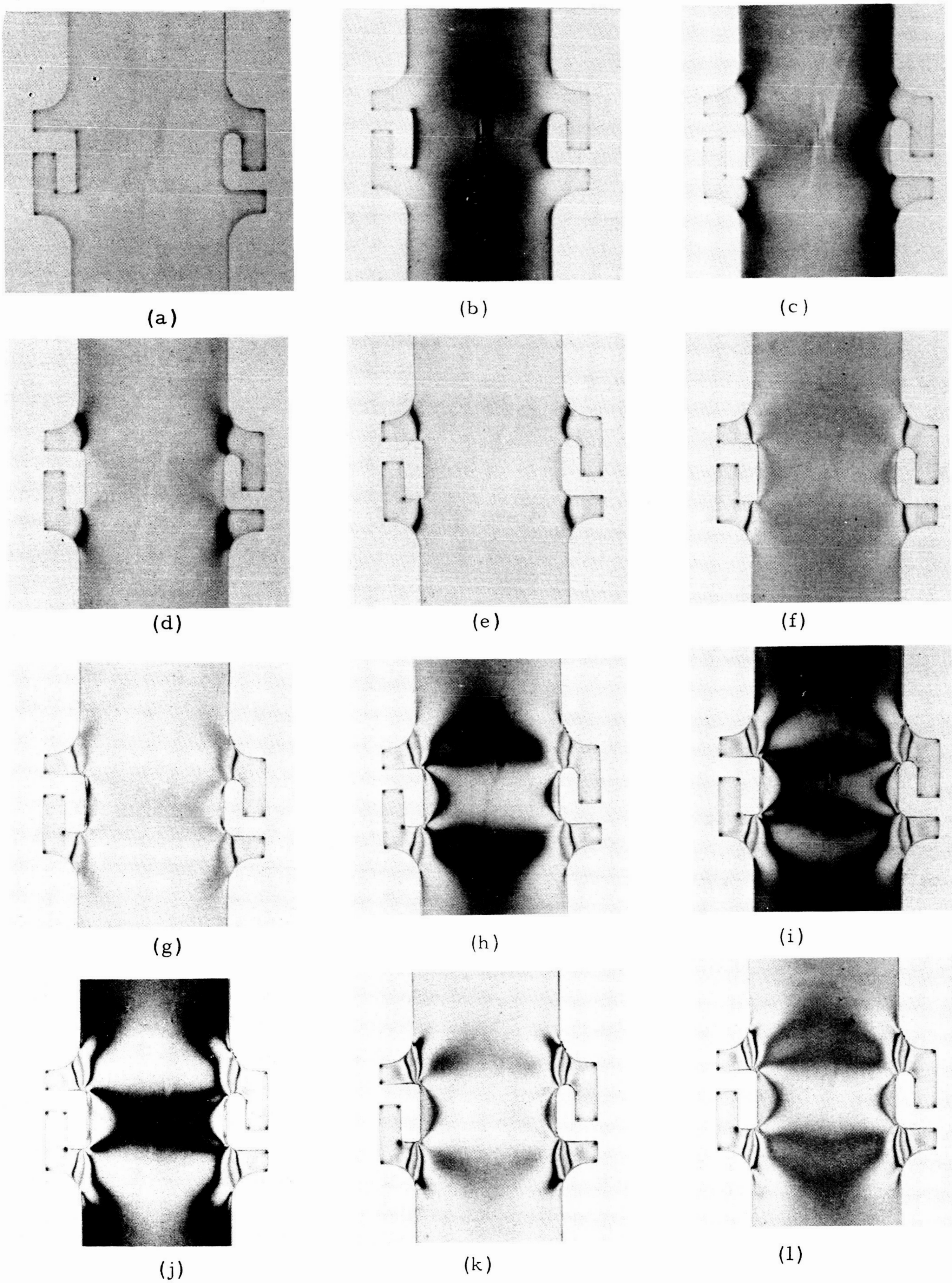


Fig. 2 STRESS PATTERN GROWTH ON HOOKED SPECIMEN. (a) INDICATED NO LOAD WHILE INCREASING LOADS ARE REPRESENTED BY (b) THROUGH (l). (2.2 X)

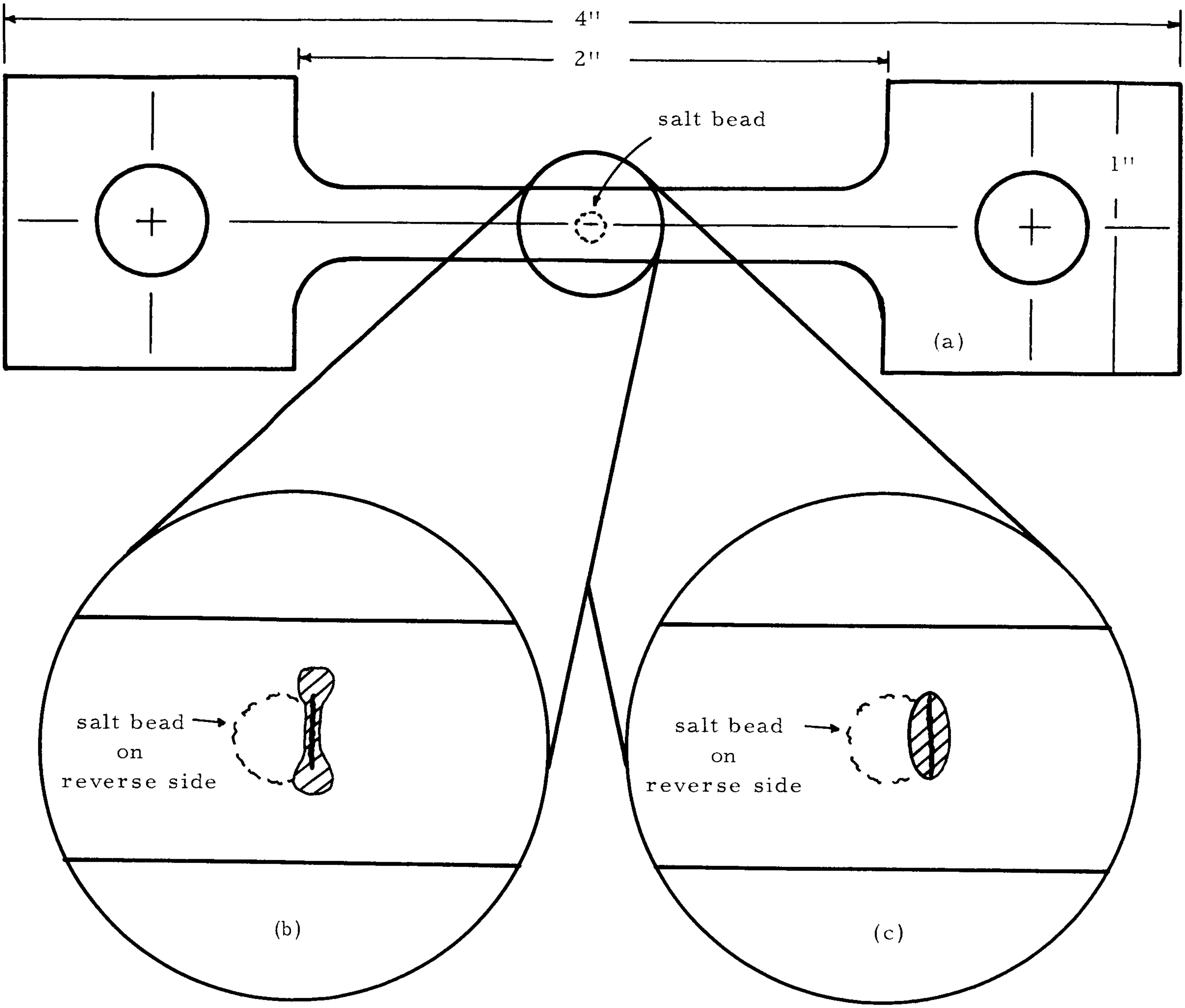
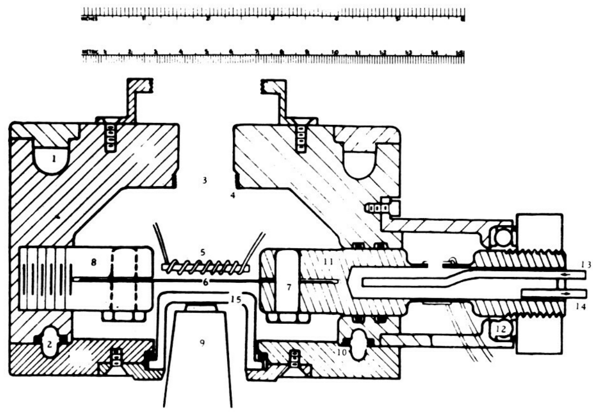
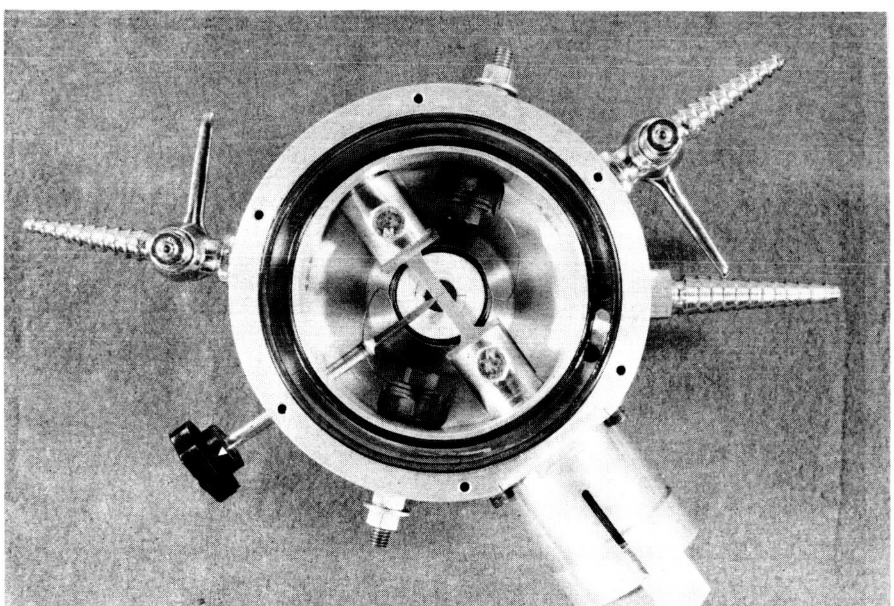


Fig. 3 (a) SMOOTH TENSILE SPECIMEN WITH SALT BEAD ON REVERSE SIDE.
(b) EXPECTED STAIN PATTERN FOR LIQUID CORROSION PRODUCTS.
(c) EXPECTED STAIN PATTERN FOR SOLID OR GASEOUS CORROSION PRODUCTS.



1. Water duct
2. Water duct
3. Vacuum aperature
4. 3000°F hearth seat
5. Nichrome heating element
6. Tensile specimen
7. Pin
8. Stationary grip
9. Long working distance microscope objective
10. "O"-ring
11. Load cell and tensile grip
12. Thrust bearing
13. Water inlet
14. Water outlet
15. Quartz window

(a)



(b)

Fig. 4 (a) SCHEMATIC DRAWING OF TENSILE HOT STAGE (Side View)
(b) PHOTOGRAPH OF INTERIOR OF HOT STAGE (Top View)

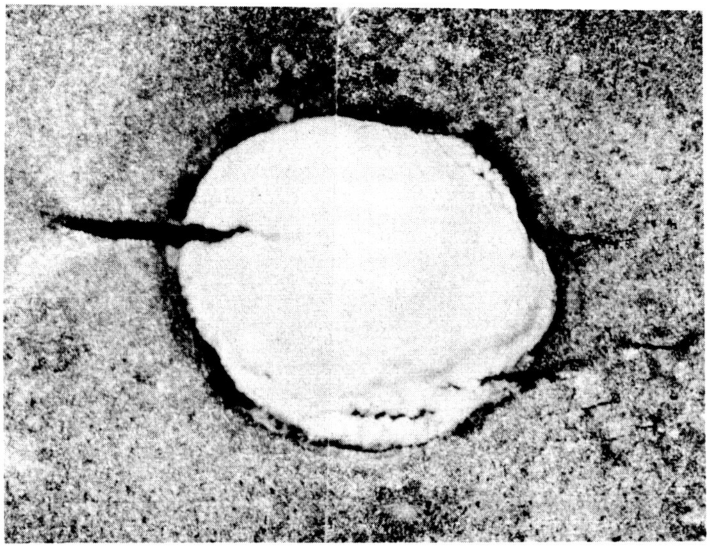


Fig. 5 SMOOTH TENSILE SPECIMEN OF Ti-6Al-4V. (EXPOSED 3 HOURS AT 650^{o}F AND 80 KSI. SPECIMEN ETCHED BEFORE APPLYING SEA-SALT SLURRY.) (~ 20 X)

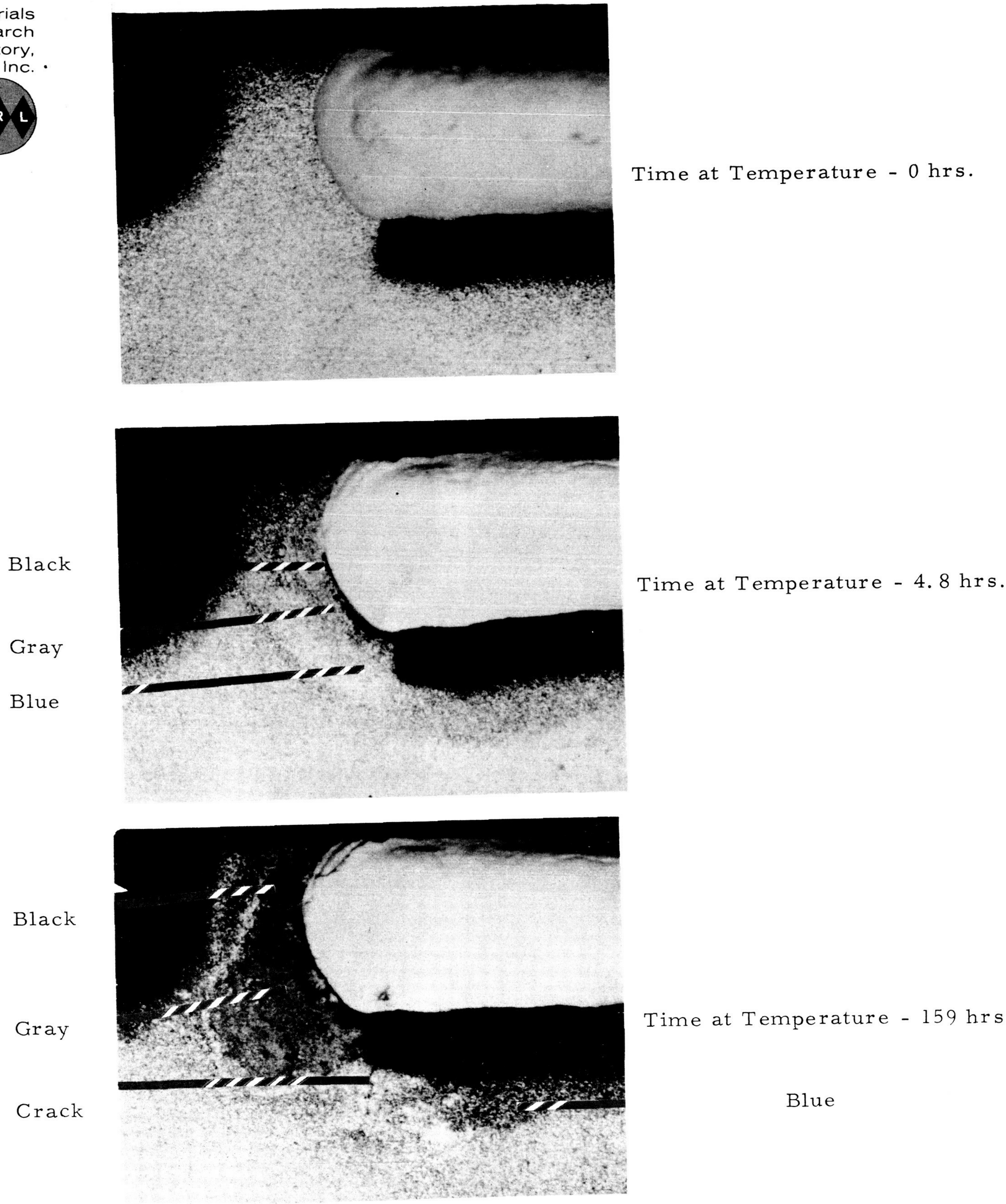


Fig. 6 LAPSED TIME PHOTOGRAPHS OF CORROSION PRODUCTS IN VICINITY OF HOOKS. (Ti-8Al-1Mo-1V ALLOY, NATURAL SEA SALT, $650^{\circ}F$ EXPOSURE - 50,000 psi.) (25X.)

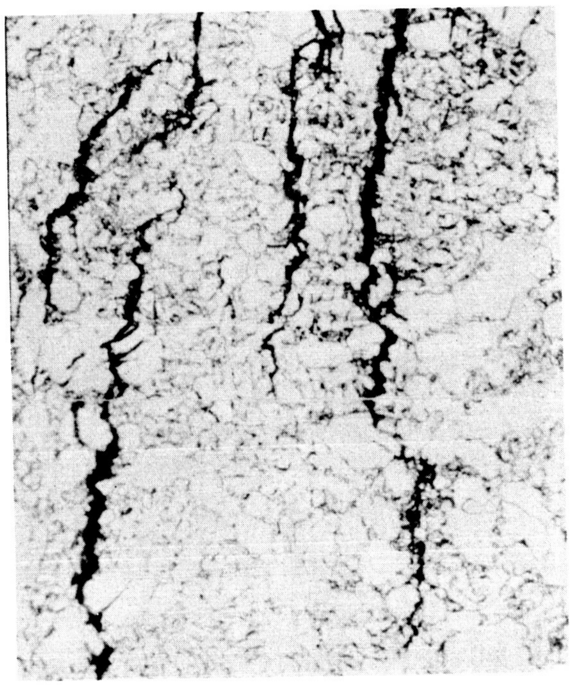


Fig. 7 TYPICAL INTERGRANULAR CRACKING OCCURRING AT POINT P_1
(Ti-6Al-4V, 80,000 psi, 650°F, 100 hrs.)
(~500 X)

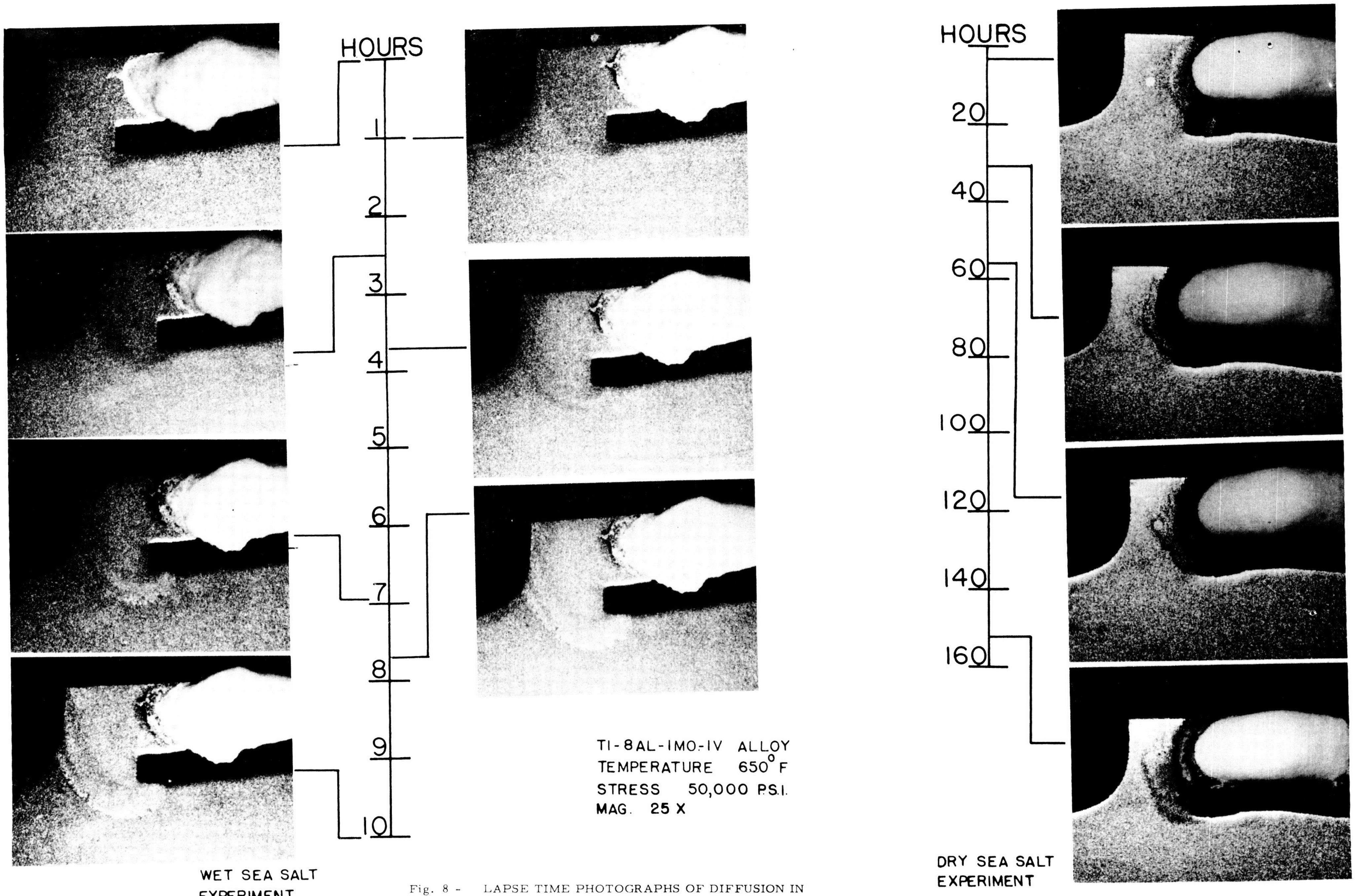


Fig. 8 - LAPSE TIME PHOTOGRAPHS OF DIFFUSION IN A "WET" AND "DRY" TEST.

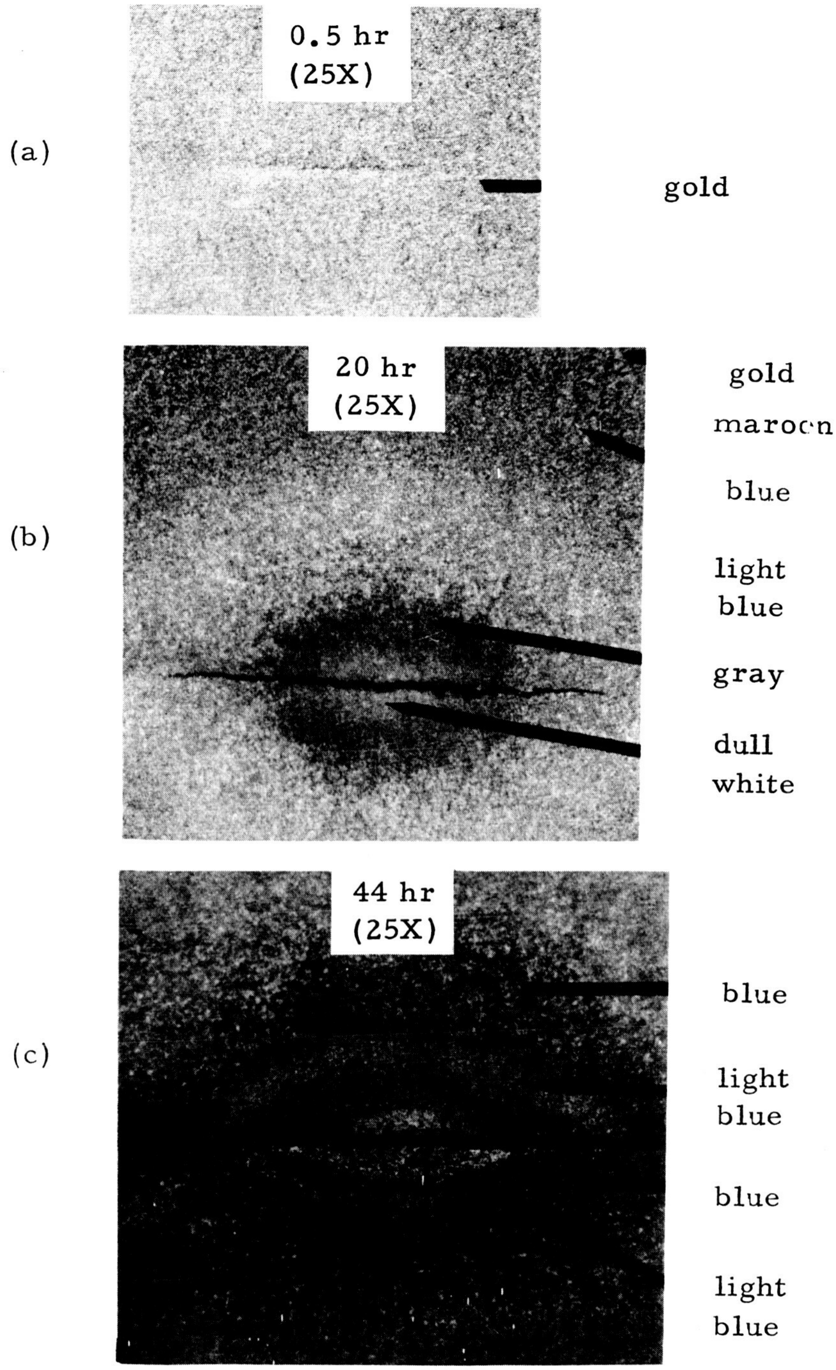


Fig. 9 DEVELOPMENT OF CRACK AND DIFFUSION OF CORROSION PRODUCTS THROUGH IT IN Ti-6Al-4V

(a) First indication of crack on back side of salt bead, 650 ^{o}F, 60,000 psi

(b) Stain pattern after 20 hours, 650 ^{o}F, stress decreased to 52,000 psi to slow down crack extension

(c) Stain pattern after 44 hours, temperature increased to 875 ^{o}F, stress decreased to 4,000 psi

Materials
Research
Laboratory,
Inc.

24

N66-16195

PART II

ELECTROCHEMICAL ASPECTS OF HOT SOLID SALT STRESS CORROSION CRACKING OF TITANIUM BASE ALLOY

ABSTRACT

16195

It is shown that the corrosion of titanium in the presence of hot solid salt occurs due to an oxygen differential cell. Cracking always occurs at the cathode of this cell, and the cracking can be prevented by impressing an anodic current on the stressed specimen.

Author

INTRODUCTION

Because titanium base alloys have an excellent strength to weight ratio with a high fracture toughness in the temperature range of 400 - 800°F, they are among the most promising structural materials for use in this temperature range. This promise, however, is clouded by the susceptibility of the alloys to stress corrosion cracking in the presence of hot solid salt in laboratory tests. Eventual elimination of the problem, as well as the immediate need to design structures which avoid the embrittlement requires a better understanding of the mechanism of the susceptibility.

One unique aspect of the stress corrosion cracking of these alloys is its apparent insensitivity to initial stress concentrators. When sharply edge notched specimens, with the dimensions shown in Fig. 1a, were heavily salt coated in the vicinity of the notch, as shown schematically in Fig. 1b, and exposed at 650°F to a nominal stress of 25,000 psi (calculated on the basis of the notch section area), they cracked at the edge of the salt layer, Fig. 1c, rather than across the notch plane where the stress is far higher due to both the reduced cross-section and the stress concentration (1)*. Since the specimens crack at the location of lower stress, it might be assumed that cracking is independent of applied stress. This is shown not to be the case, however, by the smooth tensile specimen exposure data in Fig. 2. Hence it must be assumed that stress corrosion cracks can form only at the edge of the salt layer, and the loss in load carrying capacity at this location is far greater than the strength reduction produced by the mechanical notch.

Examination of many specimens containing only a single salt bead show that crack initiation is always limited to the salt-metal-air interface, Fig. 3, where a gray corrosion product forms (3). The fact that cracking is restricted to this single site suggests that the fracture is associated with an electrochemical mechanism in which the metal near the edge of the salt bead is always one electrode of the cell.

* Numbers in parentheses refer to reference at end of report.

This study was undertaken to investigate this and other electrochemical features of cracking. Three types of experiments were conducted. In the first of these, the appearance of the metal in the vicinity of a salt bead was examined after high temperature exposure in the absence of stress. In the second, an oxygen differential cell was used to measure the potential between an air exposed and an air deficient specimen, and in the third, salt coated specimens were made the anodes or cathodes of a Ti-salt-Ti cell and then exposed to stress at an elevated temperature in order to determine the influence of an impressed emf on fracturing.

MATERIALS

The titanium alloy, Ti-8Al-1Mo-1V was used throughout this study. It was supplied as 0.018 inch thick sheet in the mill annealed condition, so that it was probably free of residual stresses. The corroding medium was solid natural sea salt. The latter was made by evaporating natural sea water to the consistency of a thick paste. The slurry was applied to the specimens, either as small beads or as a thick coating in this study.

TEST RESULTS

Salt Drop Experiments

The location of anode and cathode in a corroding metal system can be identified by the appearance of the metal after it has been in contact with a drop of the corroding agent. At the anode, metal is dissolved, i.e.

$$M = M^{+} + e$$

while at the cathode, oxygen is reduced,

$$2e + O = O^{--}$$

For this reason, small beads of a slurry of natural sea salt were placed on metallographically polished surfaces of Ti-8Al-1Mo-1V alloy and heated to 800^{o}F for 5 hours in the absence of stress. The polishing was necessary to have a smooth enough surface for subsequent microscopic observation and the absence of a stress was to prevent catastrophic failure. After the high temperature exposure, the salt and corrosion products were carefully washed off, and the metal in the vicinity of the original salt bead had the appearance shown in Fig. 4. Note that under the center section of the bead, where air was excluded, the metal was dissolved indicating an anodic reaction. At the periphery of the salt bead the oxide appears to have been stripped implying a cathode reaction. The appearance of the pit in relationship to the original salt bead is more clearly seen in Fig. 5. Note that in short exposure times metal is dissolved only under the center of the bead where oxygen is most completely excluded. The spottiness of the pit probably results because some oxygen is dissolved in the salt solution, and the oxygen allows some cathodes to form under the salt in short exposure times. With increasing times dissolution under the center of the bead becomes more uniform much as is the case with a salt water drop on steel (4). This appearance would suggest that titanium alloys, in the presence of hot solid salt, corrodes because of an oxygen differential cell. The metal under the thickest part of the salt bead, i. e., its center, is deficient in oxygen as compared with that near the periphery.

The occurrence of a pit in the unstressed metal also indicates that the oxide can be removed simply by the presence of hot salt, and it is not necessary for a mechanical rupturing of the oxide for the salt to contact the metal. This conclusion is substantiated by previously described tests (3) in which salt beads were placed on side hooks attached to tensile specimens. Although the hooks were unstressed, a corrosion product was formed at this location, and fracturing occurred after some time when the corrosion products and/or hydrogen ions reached the stressed portion of the specimen. Although mechanical rupturing of the oxide is not required, some time is needed for its removal by the salt, presumably by the reaction of the TiO_2 with O_2 and NaCl (5). It is suggested that a major portion of the time needed to cause cracking is consumed in removal of the oxide.

Oxygen Differential Corrosion Cell

To be certain corrosion was the result of an oxygen differential, tests were also carried out in a cell in which one piece of stressed titanium was maintained in a vacuum or argon atmosphere while a second piece of titanium, exposed to the air, was in contact with the first one through a salt bridge and also connected to it electrically by a nickel wire. A schematic diagram of the cell is shown in Fig. 6, and the details of its construction have been previously described (1). When the system was heated to the vicinity of 650 to 800^{o}F, an emf varying from 1. 0 to 0. 1 volts was measured and the direction of current flow showed that the inside oxygen deficient specimen was the anode and the outside the cathode.

Effect of an Impressed emf

Since cracking only occurs in the cathodic region, it should be possible to prevent failures by making the stressed member the anode in a titanium-salt-titanium cell. This of course is opposite to the more "classical" stress corrosion cracking (e.g. austenitic steel in boiling $MgCl_2$) which is prevented by cathodic, rather than anodic protection, Fig. 7. In order to make the stressed members the anode of the cell, a small hole was drilled into the stressed section of tensile specimens, Fig. 8a. After drilling, the specimen was cleaned in acetone and then in Alconox. One side of the specimen was then coated with a thick salt slurry, and a small metal tab of the same alloy (Ti-8Al-1Mo-1V), Fig. 8b, placed over the salt, and the assembly held together with a single steel screw and nut, Fig. 8c. The fastener was insulated from the titanium surfaces by a small sheet of mica under the head of the screw and a sheet of mica and ceramic bead under the nut. The screw was prevented from touching the sides of the hole simply by making the hole considerably larger than the screw diameter.

Three groups of specimens of this type were tested by exposing them at 650°F to 50,000 psi. stress (calculated on the basis of the cross-sectional area containing the hole diameter). The specimens were tested in a creep furnace, the ends of which were plugged with an insulating material so that the atmosphere within the furnace was stagnant. An emf of 25 volts* was supplied between the specimen and attached electrode.

For six tests, the specimen was made the cathode, Fig. 9a, and as shown in Table I, fractures occurred in times between 26 and 180 hours. An additional five specimens were tested to serve as controls, Fig. 9b, in which no voltage was applied, and these failed between 2 and 155 hours. Note that most of these control specimens did not fracture at the edge of the salt layer. This resulted because air could travel through the hole to the salt coated side of the specimen since they were not coated on the back side. Hence cathodes would be expected to form both near the edge of the salt layer and the periphery of the hole. In the last series, eight stressed specimens were made the anode, Fig. 9c, and although one failed in fourteen hours, the remainder of the specimens did not fail within the total test period which varied from 225 to 864 hours. Since currents were

* One cathodic specimen had an emf of 1.5 volts applied.

not measured, during the test, it is probably that poor contact was made between the specimen, salt and electrode in the single test in which premature fracture occurred.

DISCUSSION AND CONCLUSIONS

Stress corrosion cracking of titanium alloys in the presence of hot solid salt occurs because of a product generated at the cathode of an oxygen differential cell. The metal under the center of the bead, where oxygen is less available, is the anode while the periphery of the bead is the cathode. Consequently cracks are always initiated near the salt-metal-air interface.

Mechanical rupturing of the oxide does not appear to be necessary since pits were formed in the presence of hot salt in the absence of stress. Hence, it must be assumed that the titanium oxide either reacts with the hot salt or else it is soluble in it. An appreciable amount of the time that is required for cracking to occur is probably consumed in removing the oxide so that the salt can contact the metal.

Cracking can be prevented by applying anodic protection to the stressed member. This differs from more "classical" stress corrosion cracking where fracturing is prevented by supplying cathodic, rather than anodic, protection.

The association of cracking with a cathodic corrosion product explains two commercially important observations that have been made on the characteristics of cracking. The first of these is by Heimerl, et al. (7), who showed cracking to be most severe, when the salt layer was thin. This is now to be expected since a thin salt layer is discontinuous and would form a cathode at the periphery of each salt crystal. Thick salt layers on the other hand would form cathodes only at the edge of the layer.

Piper and Fager (8) found that cracking was minimized if the exposure at the elevated temperature was cyclic rather than continuous. Their test specimens, which were soaked in a 3.5% NaCl solution, heated to 550^{o}F for 2-1/2 hours and then cooled to room temperature for 667 cycles, exhibited no stress corrosion cracking. This would suggest that within 2-1/2 hours, the titanium oxide is not completely removed by the hot salt, and the oxide would have an opportunity to reform on each cooling part of the cycle.

TABLE I

RESULTS OF INDUCED ANODE, INDUCED CATHODE AND CONTROL EXPERIMENTS

All specimens were exposed at 650°F
and stressed to 50,000 psi

Impressed Cathodes

Time, hrs.	D. C. Voltage	Failed	Did not fail
26	25	X	
34	25	X	
79	25	X	
83	25	X	
121	1.5	X	
180	25	X	

Controls

Time, hrs.	D. C. Voltage	Failed	Did not fail
2	0	X	
86	0	X	
90	0	X	
131	0	X	
155	0	X	

Impressed Anodes

Time, hrs.	D. C. Voltage	Failed	Did not fail
14	25	X	
225	"		X
225	"		X
252	"		X
252	"		X
647	"		X
864	"		X
864	"		X

REFERENCES

1. Kirchner, R. L., and Ripling, E. J., First Interim Report on Elevated Temperature Stress Corrosion of High Strength Sheet Materials in the Presence of Stress Concentrators, Contract NASr-50, November, 1964.

2. Progress Report on the Salt Corrosion of Titanium Alloys at Elevated Temperature and Stress, Battelle Memorial Institute, TML Report 88, November, 1957.

3. Kirchner, R. L., and Ripling, E. J., Diffusion of Corrosion Products in Hot Salt Stress-Corrosion Cracking of Titanium, presented at the Fifth Pacific Area National Meeting of the ASTM, Paper No. 45, November, 1965.

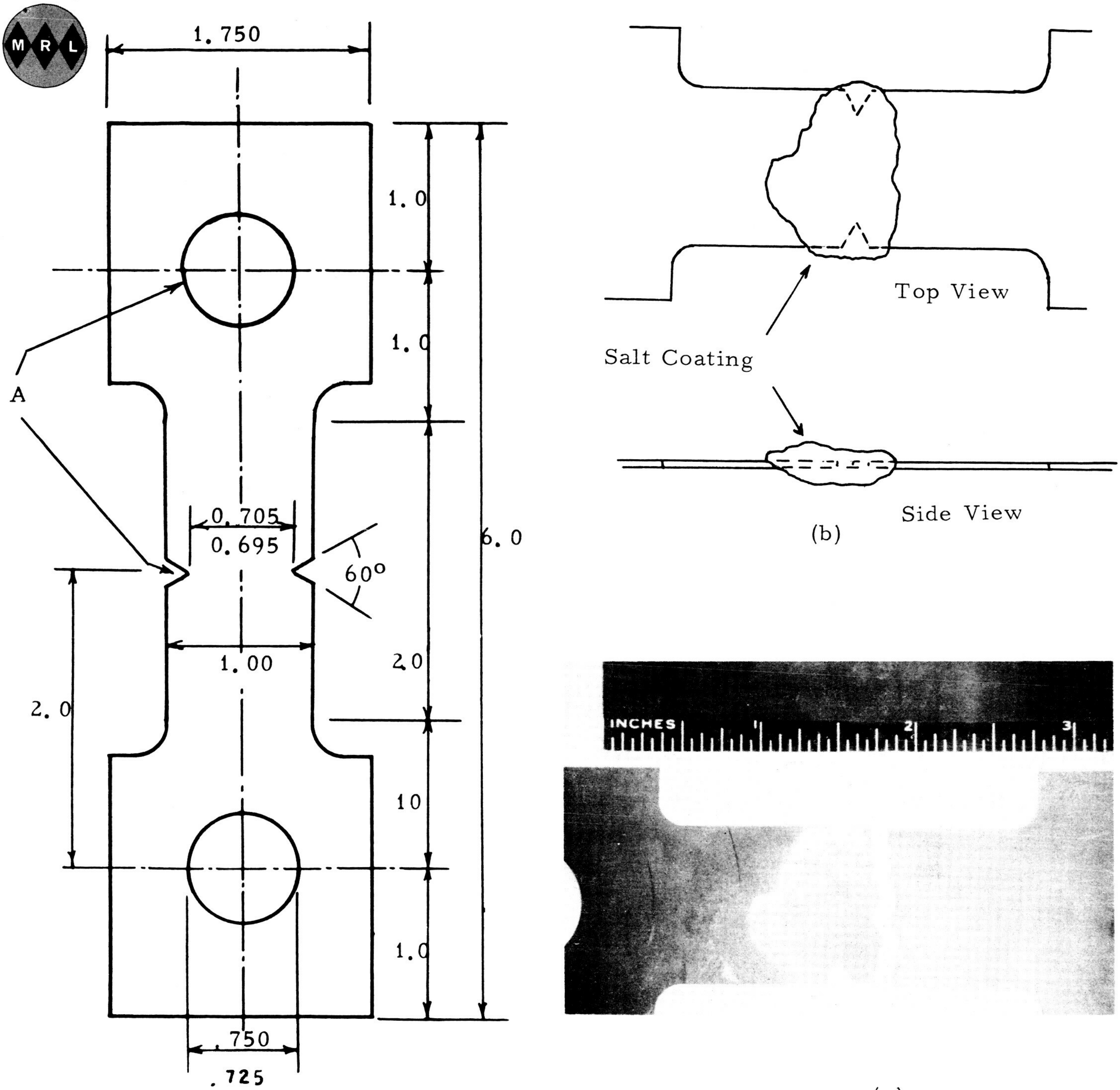
4. Evans, U. S., The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications, pp. 115-121, Edward Arnold (Publishers) Ltd., London, 1960.

5. Crossley, F. A., Reichel, C. J., and Simcoe, C. R., The Determination of the Effects of Elevated Temperatures on the Stress Corrosion Behavior of Structural Materials, WADD Technical Report 60-191, May, 1960.

6. Parkins, R. N., The Stress Corrosion Cracking of Mild Steels in Nitrate Solution, Journal of the Iron and Steel Institute, Vol. 172, pp. 149-162, 1952.

7. Heimerl, G. J., Braski, D. N., Royster, D. M., and Dexter, H. B., Salt Stress Corrosion of Ti-8Al-1Mo-1V Alloy Sheet at Elevated Temperatures, presented at the Fifth Pacific Area National Meeting of the ASTM, Paper No. 42, November, 1965.

8. Piper, D. E. and Fager, D. N., The Relative Stress Corrosion Susceptibility of Titanium Alloys in the Presence of Hot Salt, presented at the Fifth Pacific Area National Meeting of the ASTM, Paper No. 38, November, 1965



(c)

A - Surfaces true to centerline within 0.001 inch
Notch root radius less than 0.001 inch.

(a)

Fig. 1 CRACKING IN A HEAVILY COATED EDGE NOTCH SPECIMEN (1).
(a) SPECIMEN DIMENSIONS
(b) METHOD OF SALT COATING
(c) APPEARANCE OF FRACTURED SPECIMEN (Ti-8Al-1Mo-1V)

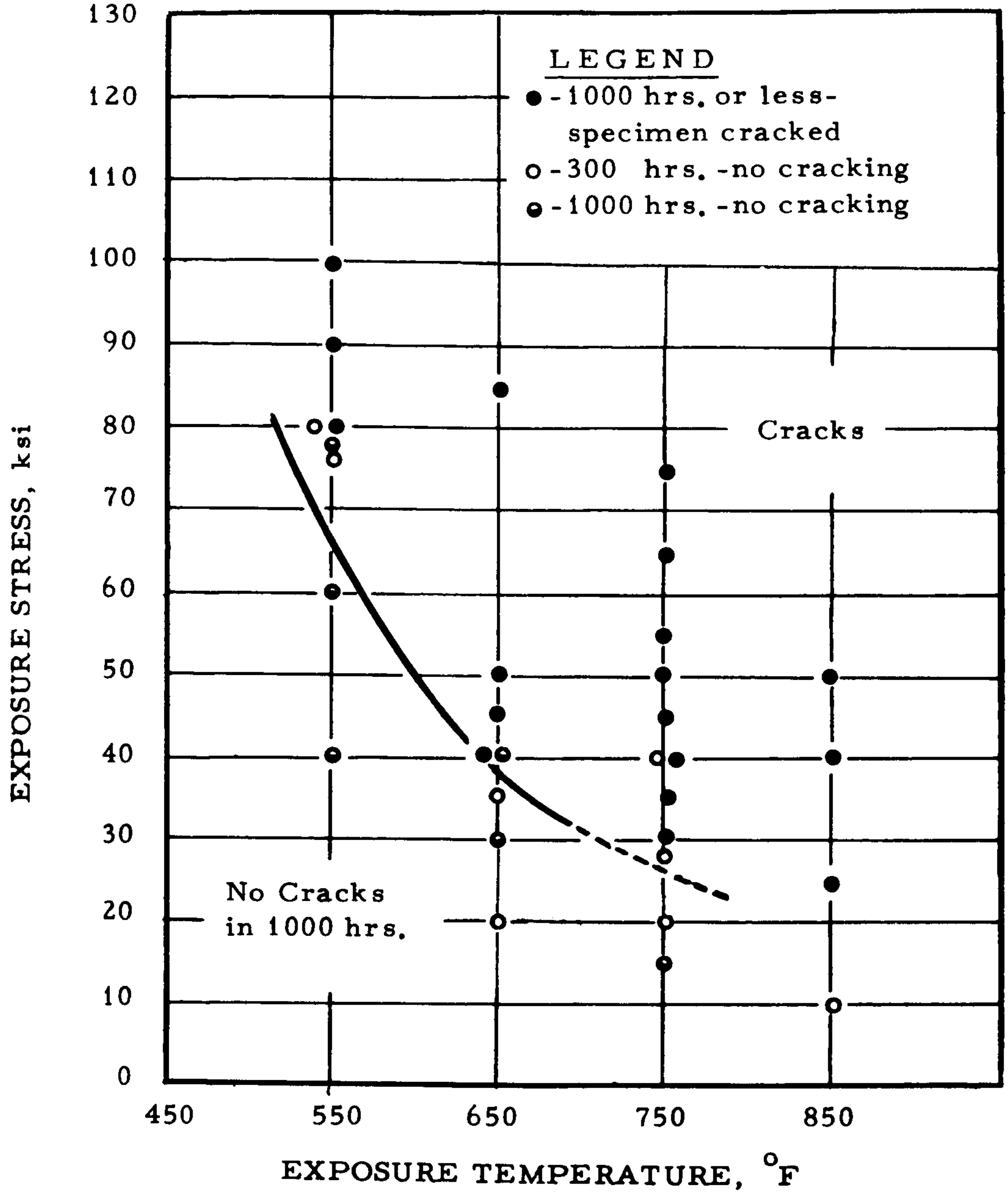


Fig. 2 EFFECT OF EXPOSURE STRESS AND TEMPERATURE ON FRACTURE OF ANNEALED Ti-6Al-4V ALLOY IN THE PRESENCE OF NaCl (2).

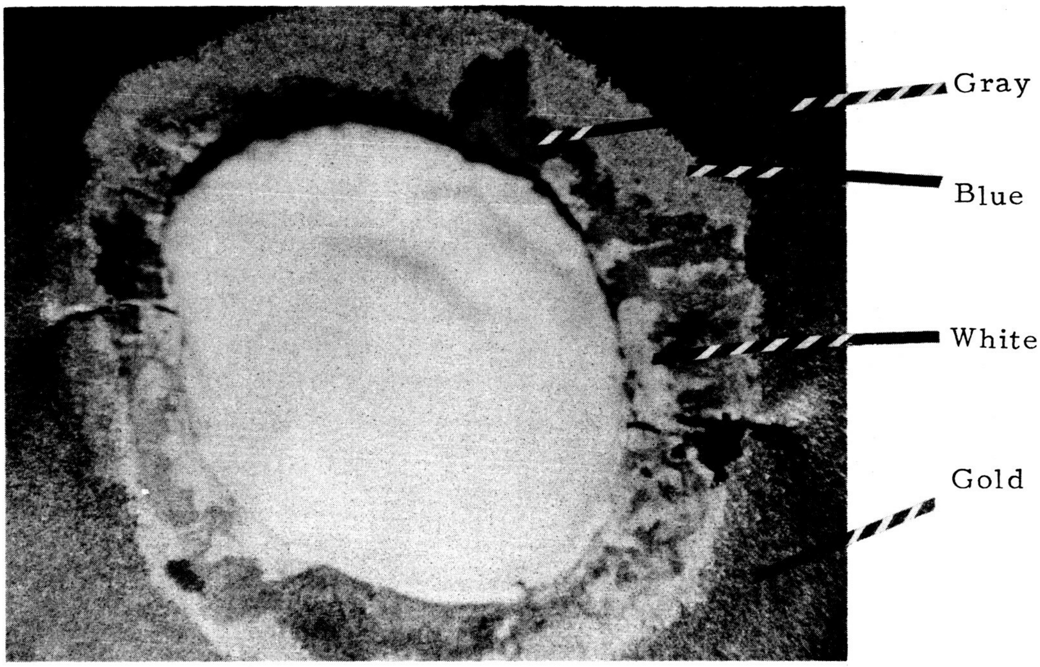


Fig. 3 CRACKING IN THE VICINITY OF THE SOLID BEAD (Ti-8Al-1Mo-1V, EXPOSED 25 HOURS AT 650°F AND 70 ksi. SPECIMEN ETCHED BEFORE APPLYING SEA SALT SLURRY.) (25 X)

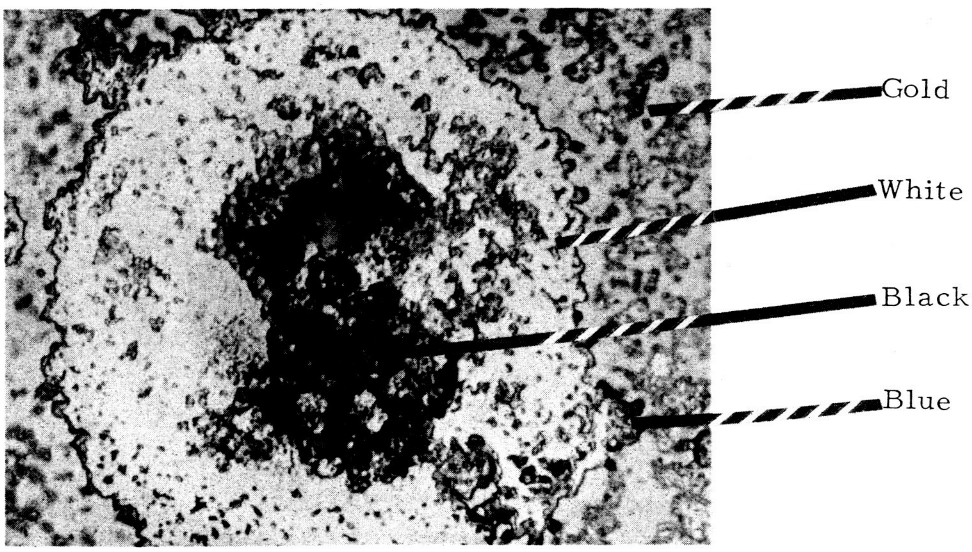
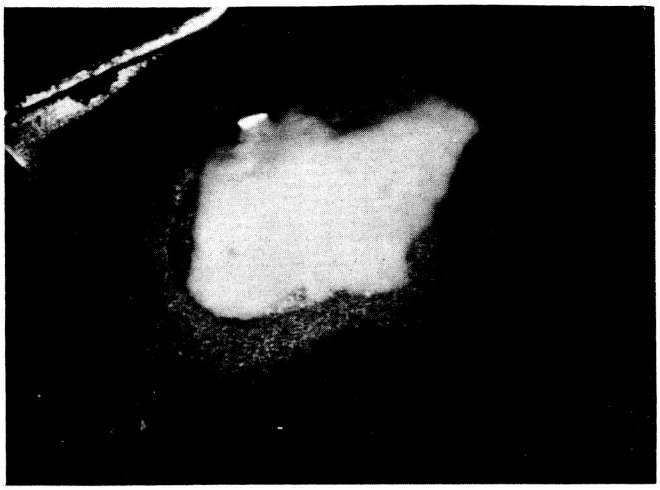
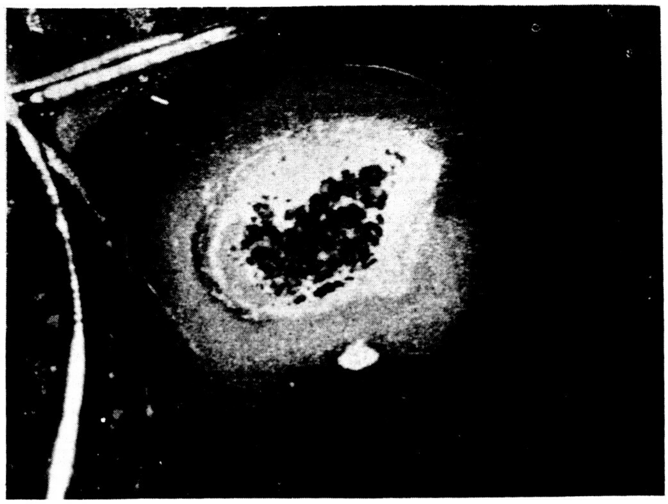


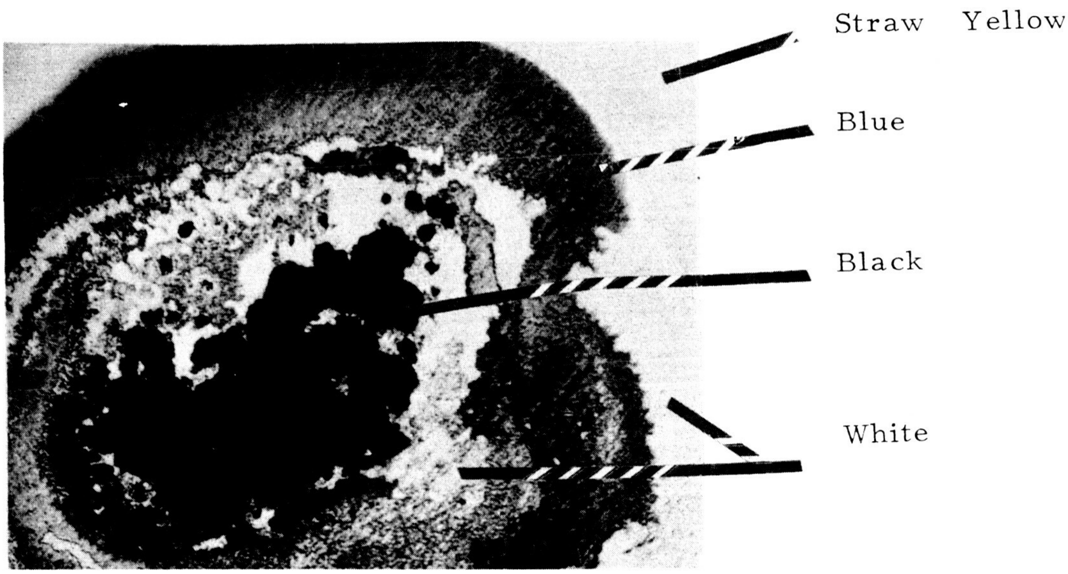
Fig. 4 APPEARANCE OF CORROSION PIT IN UNSTRESSED Ti-8Al-1Mo-1V SPECIMEN AFTER 5 HOURS AT 800°F. (260 X)



(a)



(b)



(c)

Fig. 5 SURFACE ATTACK OF SEA SALT ON UNSTRESSED Ti-8Al-1Mo-1V SPECIMEN.

(a) APPEARANCE OF SALT BEAD AND CORROSION PRODUCTS AFTER BEING EXPOSED AT 800°F FOR 5 HOURS (25 X).

(b) SURFACE ATTACK AFTER REMOVAL OF SALT AND CORROSION PRODUCTS (25 X).

(c) ENLARGED VIEW OF ATTACKED AREA (50 X).

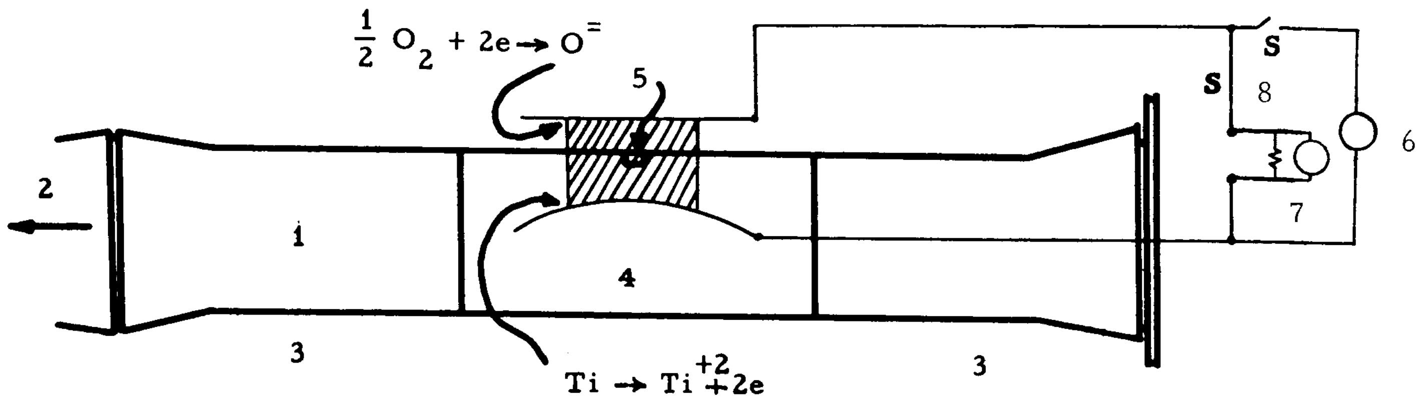


Fig. 6 SCHEMATIC DIAGRAM OF CONTROLLED ATMOSPHERE CORROSION CELL.

1. Vacuum or argon chamber
2. To vacuum or argon
3. Glass ends of 4 inch diameter tube
4. Glazed alundum tube sealed to glass (glazed to prevent porosity)
5. Unglazed area on tube permeated with salt
6. Vacuum tube volt meter
7. L & N mv. recorder
8. Precision resistor

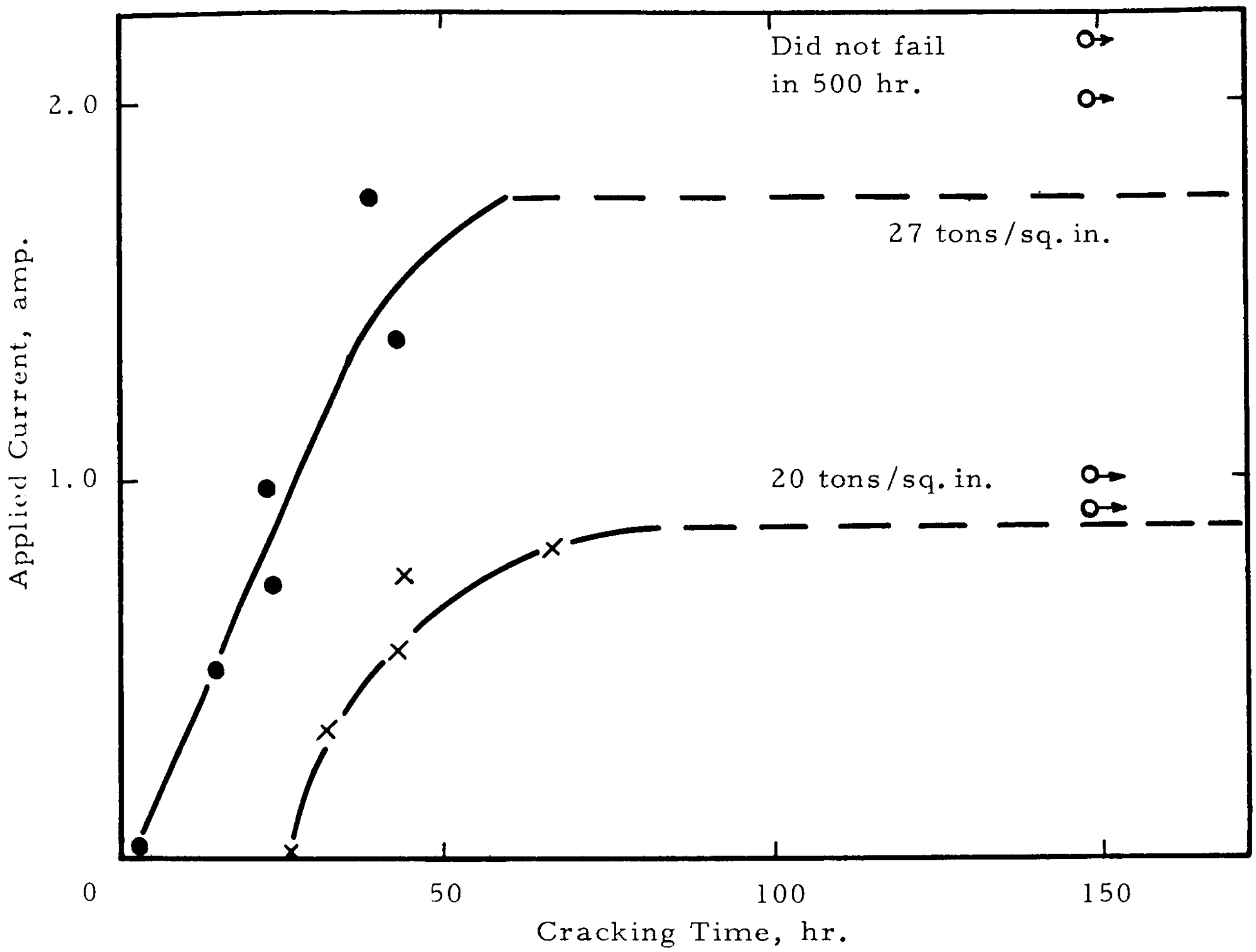


Fig. 7 EFFECT OF CATHODIC PROTECTION ON THE CRACKING TIME OF A MILD STEEL (6).
(In a solution of calcium nitrate (860 g./l.) and ammonium nitrate (30 g./l.))

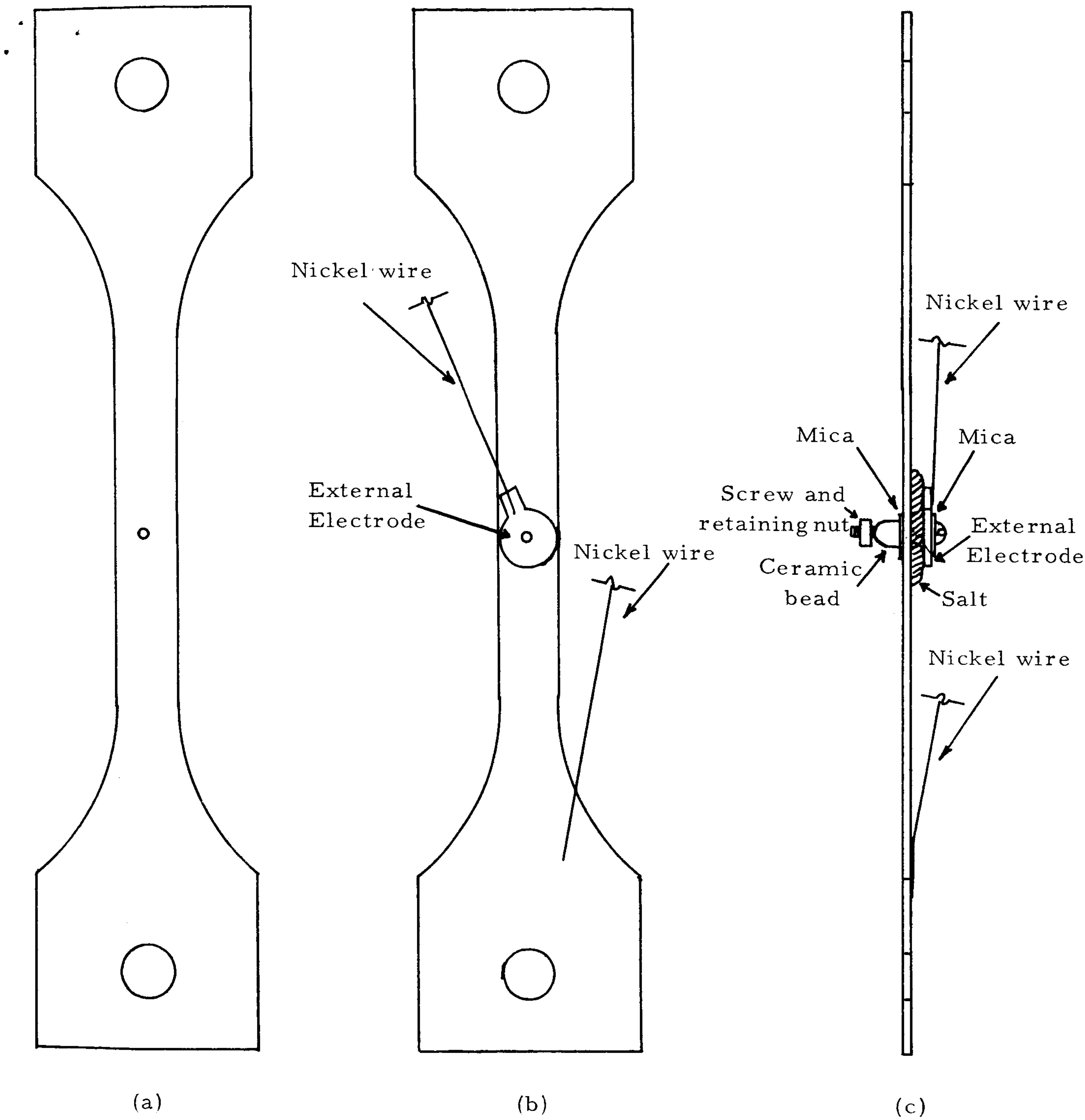
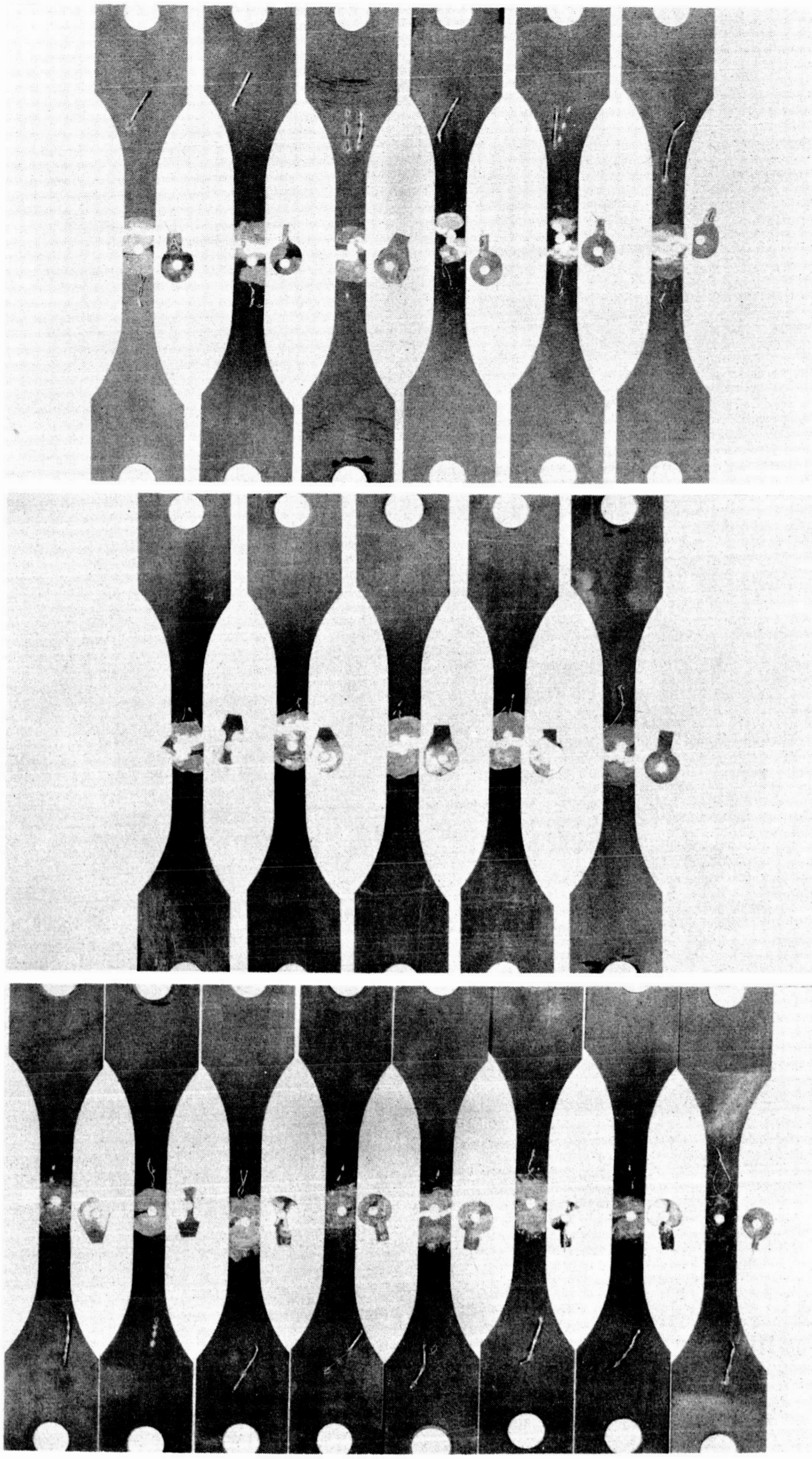


Fig. 8 DIAGRAM OF THE IMPRESSED ANODE AND CATHODE SPECIMENS.

(a) TENSILE SPECIMEN WITH HOLE.

(b) TENSILE SPECIMEN WITH EXTERNAL ELECTRODE AND WIRES ATTACHED.

(c) SIDE VIEW OF THE TENSILE SPECIMEN SHOWING THE DETAILED CONSTRUCTION OF THE TITANIUM-SALT-TITANIUM CELL.



(a)

(b)

(c)

Fig. 9 APPEARANCE OF IMPRESSED EMF SPECIMENS AFTER TESTING:

(a) IMPRESSED CATHODE SPECIMENS AFTER EXPOSURE TO 650°F AND 50,000 psi UNTIL FAILURE

(b) CONTROL SPECIMENS AFTER EXPOSURE TO 650°F AND 50,000 psi UNTIL FAILURE

(c) IMPRESSED ANODE SPECIMENS AFTER EXPOSURE TO 650°F AND 50,000 psi UNTIL TEST WAS STOPPED.

PART III

MISCELLANEOUS EXPERIMENTS

Oxygen Differential Corrosion Cell

Some additional tests also were continued on the oxygen differential corrosion cell during the past year. In the previously reported work on this equipment, test results were scattered, that is, in some experiments the coupled sample failed; in others, the uncoupled sample failed, but more commonly either both or neither sample cracked. It was assumed that this was a result of oxygen seepage into the test chamber so that local action corrosion cells overrode the influence of coupling.

To eliminate seepage, a positive pressure of purified argon was adopted for the system rather than a vacuum. With this additional modification it was found that the most important factor in causing cracking was the water content of the cell. The system modification, however, did not eliminate the scatter and it was because of these results obtained in the improved cell that it was found that corrosion was only occurring at the cathode. After realizing that cracking only appeared at cathodic regions of the cell, work with the differential cell was discontinued. However, to have reliable voltage measurements between the cathode and anode one important experiment was carried out. It will be recalled that measurements made in the past showed that the inside sample of the cell was always the anode, and the outside always the cathode. The outside specimen, however, was always unstressed and the inside specimen stressed. To be sure that the measured emf was caused by the oxygen differential and not the result of a stress difference, one experiment was performed in which the external electrodes were stressed to the same level as the internal specimens. Voltage measurements were made and an emf of the same magnitude as that found in the previous experiments was measured. Hence, it was shown that an oxygen deficiency caused the anodic reaction.

X-Ray Experiments

Numerous attempts have been made to identify the corrosion products by this laboratory and by others by using X-ray diffraction techniques. There are two problems in carrying out such experiments:

1. The corrosion products are thin so that a sharp diffraction pattern of this material cannot be obtained. In addition, the diffraction lines obtained on the underlying titanium overshadowed those obtained on the corrosion product.

2. The corrosion products formed at a high temperature are probably unstable and change in the process of cooling to room temperature.

In order to overcome these problems, hot stage diffraction measurements were made on a mixture of 28 w/o Ti-8Al-1Mo-1V powder with reagent grade NaCl. The obvious advantages of the corrosion of Ti powder is the increase in the amount of corrosion products in the area examined.

In the first experiment, the powder mixture was held at $850^{\circ}F$ for 48 hours with diffraction patterns taken periodically during the exposure. No significant changes occurred during this test. A second experiment was conducted at $950^{\circ}F$ in a moist oxygen atmosphere after 30 hours. The moisture was obtained by bubbling the oxygen through a water vessel which was heated to $190^{\circ}F$. Significant changes occurred in the diffraction patterns which indicated that rutile (TiO_2) was formed.

Also an additional pattern which could not be positively identified with the exception of one peak, d = 2.73A at $950^{\circ}F$, which corresponded to the strongest $TiCl_2$ line, d = 2.68 at room temperature, appeared.

X-Ray Analysis of Corrosion Products

The corrosion products formed on Ti-6Al-4V alloy in a Li-KCl environment during an exposure at $625^{\circ}F$ in the corrosion cell were analyzed. A Debye Scherer photograph in which copper $K\alpha$ radiation was used revealed that only KCl, LiCl and TiO_2 (Anatase) were present. The difference in the structure of the TiO_2 from that formed in the hot stage X-ray experiments was attributed to the lower temperature of formation.

Dissimilar Tabs

Salt drop experiments have revealed that commercially pure titanium corrodes in the same way as the Ti-6Al-4V and the Ti-8Al-1Mo-1V alloys. It has been generally accepted that commercially pure titanium is not sensitive to stress corrosion in the presence of hot dry salt. An experiment in which corrosion product generated on the alloys would be transferred to a stressed commercially pure titanium should provide information on the influence of alloying elements in the corrosion product on cracking. Similarly an experiment in which corrosion products generated on pure titanium would be transferred to a stressed alloy would provide information on the effects of alloy elements in the alloys.

Such experiments could be conducted by using hooked specimens of the type described in Part I of this report. For these tests, specimens were prepared by first machining smooth tensile samples. Tabs of the alloy were then electron beam welded onto specimens made from commercially pure titanium, and commercially pure tabs welded onto alloy specimens. The tabs were then further machined to form the hooks and fingers. The specimens now consisted of a pure metal or alloy stressed member with hooks and fingers of the second metal.

Two tests have been conducted to date using dissimilar metal tabs. One test was run on a commercially pure titanium tensile specimen with Ti-8Al-1Mo-1V alloy arms. Sea salt was placed on the arms and the test was conducted in a wet atmosphere at 830^{o}F with an applied load of 20,000 psi for 160 hours. The other test was conducted on a Ti-8Al-1Mo-1V alloy tensile specimen with commercially pure titanium arms. The experiment was similar to the above, but the load was 50,000 psi and the test was run for 53 hours.

The sample shown in Fig. 1 was cut so that the salt bead and the stressed section were not in the heat affected zone of the weld. Consequently, the salt bead was a relatively large distance from the tensile specimen and a long diffusion path of the corrosion products was required.

In the tests conducted to date, very little corrosive product has reached the stressed area of the sample and no cracking has occurred.

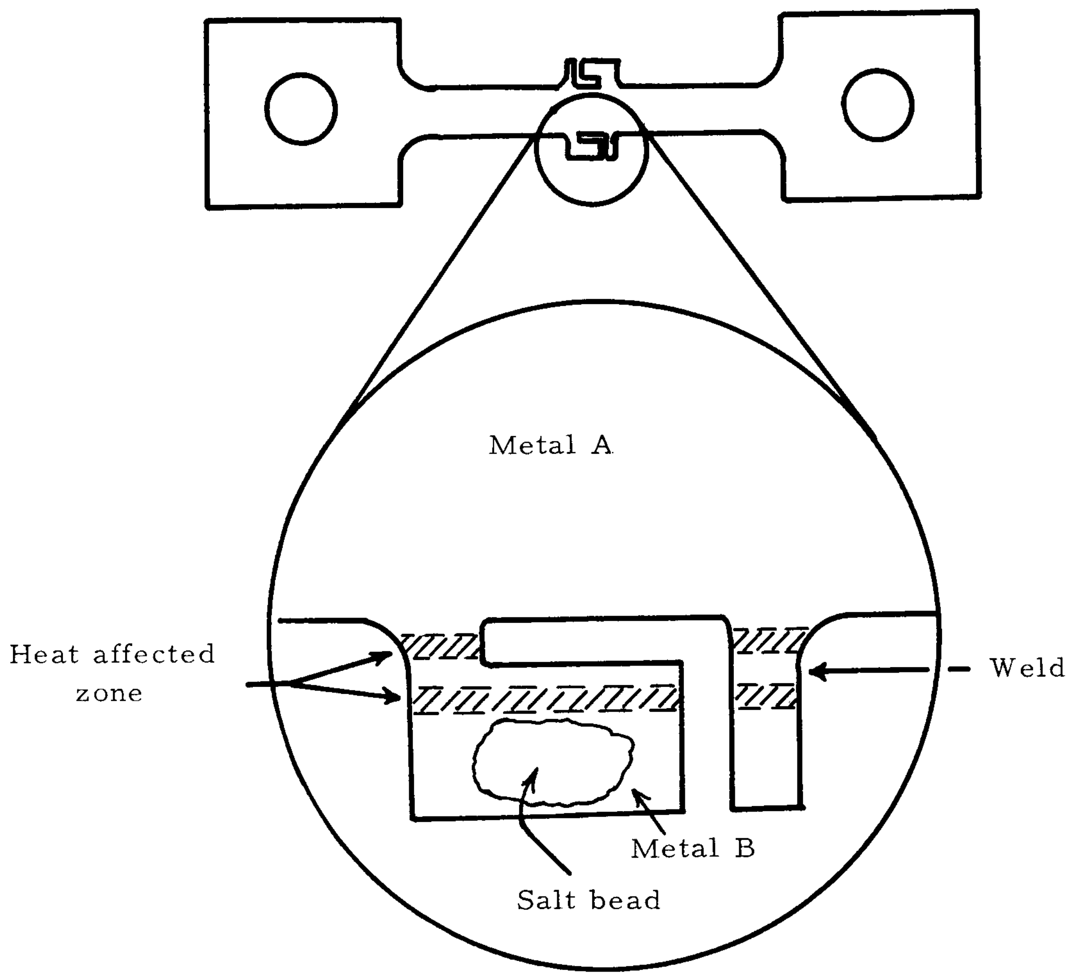


Fig. 1 TENSILE SPECIMEN WITH WELDED SIDE HOOKS.